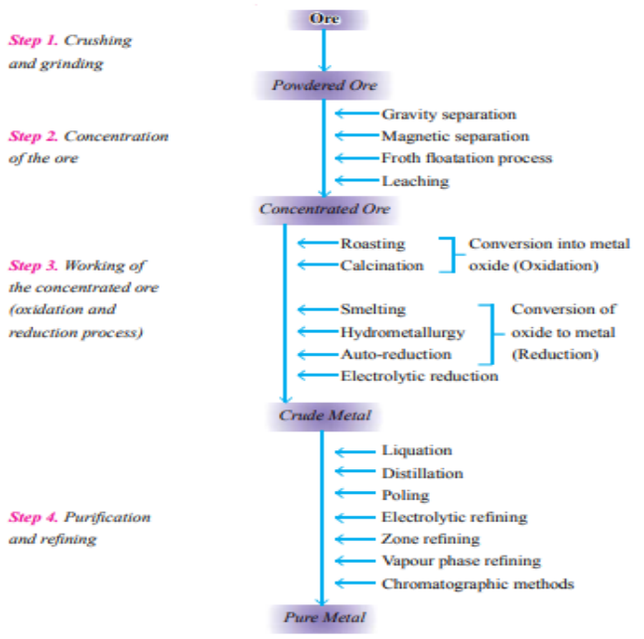
16

OCCURRENCE AND EXTRACTION OF METALS

- Metals play an extremely useful role in day-to-day life.
- Most metals are found in nature in combined form. Only a few noble metals such as gold, silver, occur in nature in free state,
- The process of extraction of metals from their ores is called metallurgical process.

Flow-sheet diagram of metallurgical process is given below



OCCURRENCE OF METALS

- Earth crust is the source of many elements. Out of these elements, 70% are metals. Aluminium is the most abundant metal of earth crust and iron comes second. The percentage of different elements in earth crust are O-49%, Si-26%, Al-7.5%, Fe-4.2%, Ca-3.2%, Na-2.4%, K-2.3%, Mg-2.3%, H-l% Metals occur in two forms in nature

(i) In native state

(ii) In combined state, depending upon their chemical reactivities.

- **Native State:** Elements which have low chemical reactivity or noble metals having least electropositive character are not attacked by oxygen, moisture and CO_2 of the air. These elements, therefore, occur in the Free State or in the native state, e.g., Au, Ag, Pt, S, O, N, noble gases, etc.
- **Combined State:** Highly reactive elements such as F, CI, Na, K, etc., occur in nature combined form as their compounds such as oxides, carbonates sulphides, halides, etc. Hydrogen is the only non-metal which exists in oxidized form only.
- **Minerals and Ores:** The naturally occurring substances in the form of which the metals occur in the earth crust are called minerals. Every mineral is not suitable for the extraction of the metal. The mineral from which the metal is economically and conveniently extracted is called an ore. Thus, ***all ores are minerals but all minerals are not ores***.
- **Gangue or Matrix:** Impurities associated with ores are called gangue or matrix.

GENERAL PRINCIPLES OF EXTRACTION OF METALS

- **Metallurgy:** The entire scientific and technological process used for isolation of the metal from its ores is known as metallurgy.

Types of Metallurgical Processes

1. Pyrometallurgy Extraction of metals takes place at very high temperature. Cu,

Fe, Zn, Sn, etc. are extracted by this method.

2. **Bydrometallurgical process** In this method, metals are extracted by the use of their aqueous solution. Ag and Au are extracted by this method.
3. **Electrometallurgical process** Na, K, Li, Ca, etc., are extracted from their molten salt solution through electrolytic method.

Steps Involved in Metallurgy

- Following steps are involved in the metallurgy:

Crushing and Pulverization

- **Crushing of the Ore:** The big lumps of ore are crushed into smaller pieces with the help of jaw-crushers. The process of grinding the crushed ore into fine powder with the help of the stamp mills is called pulverization.

Concentration or Dressing of the Ore

- **Concentration of Ores:** Removal of unwanted materials (e.g., sand. clays, etc.) from the ore is known as ore concentration, ore dressing or ore benefaction. It can be carried out by various ways depending upon the nature of the ore.

(i) Hydraulic Washing/Gravity Separation /Levigation: The process by which lighter earthy impurities are removed from the heavier ore particles by washing with water is called levigation. The lighter impurities are washed away. Thus this method is based on the difference in the densities (specific gravities) of ore and gangue.

(ii) Electromagnetic Separation: This method of concentration is employed when either the ore or the impurities associated with it are magnetic in nature. e.g., chromite, $FeCr_2O_4$, containing magnetic Silicious gangue and wolframite $FeWO_4$, Containing cassiterite, SnO_4 (non-magnetic impurities) can be separated by this method.

(iii) Froth Floatation: This method is used for the concentration of sulphide ores. This method is based on the preferential wetting of ore particles by oil and that of gangue by water. As a result the ore particles become light and rise to the top in the form of froth while the gangue particles become heavy and settle down. Thus adsorption is involved in this method. The froth can be stabilised by the addition of stabilisers (aniline or cresols).

(iv) Chemical Method-Leaching: Leaching is the process in which the ore is concentrated by chemical reaction with a suitable reagent which dissolves the ore but not the impurities, e.g., bauxite is leached with a hot concentrated solution of NaOH which dissolves aluminium while other oxides (Fe_2O_3, TiO_2, SiO_2), remain undissolved and noble metals (Ag and Au) are leached with a dilute aqueous solution of NaCN or KCN in the presence of air.

$$\underset{\text{bauxite}}{Al_2O_3 \cdot 2H_2O} + 2NaOH \longrightarrow \underset{\text{sod. meta aluminate}}{2NaAlO_2} + 3H_2O$$

$$\underset{\text{argentite}}{Ag_2S} + 4NaCN \longrightarrow \underset{\text{sod. argento cyanide}}{2Na[Ag(CN)_2]} + Na_2S$$

Calcination and Roasting of the Ore

- The concentrated ore is converted into metal oxide by calcination or roasting.

(i) Calcination: It is the process of converting an ore into its oxides by heating it strongly, below its melting point in a limited supply of air or in absence of air. During calcination, volatile impurities as well as organic

matter and moisture are removed. Calcination is used for metal carbonates and hydroxides and is carried out in reverberatory furnace.

$$Al_2O_3 \cdot 2H_2O \xrightarrow{Heat} \underset{\text{alumina}}{Al_2O_3} + 2H_2O$$

$$\underset{\text{limestone}}{CaCO_3} \xrightarrow{Heat} CaO + CO_2$$

$$\underset{\text{dolomite}}{CaCO_3 \cdot MgCO_3} \xrightarrow{Heat} CaO + MgO + 2CO_2$$

(ii) Roasting: It is the process of converting an ore into its metallic oxide by heating it strongly below its melting point m excess of air. This process is commonly used for sulphide ores and is carried out in blast furnace or reverberatory furnace. Roasting helps to remove the non-metallic impurities and moisture.

$$2ZnS + 2O_2 \longrightarrow 2ZnO + 2SO_2\uparrow$$
$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2\uparrow$$

Reduction of the Metal Oxides to Free Metal

- This process is carried out after calcination or roasting of ores. In this process called smelting, the oxide ores are converted into the metallic state by reduction

(A) Smelting (reduction with carbon): The process of extracting the metal by fusion of its oxide ore with carbon (C) or CO is called smelting. It is carried out in a reverberatory furnace. For Example:

$$ZnO + C \longrightarrow Zn + CO\uparrow$$
$$Fe_2O_3 + CO \xrightarrow{823\ K} 2FeO + CO_2$$
$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO\uparrow$$

- During smelting a substance called flux is added which removes the non-fusible impurities as fusible slag. This slag is insoluble in the molten metal and is lighter than the molten metal. So, it floats over the molten metal and is skimmed off.

(i) By using carbon as a reducing agent: This method is used for the isolation of iron, tin and zinc metals from their respective oxides.

$$SnO_2 + 2C \longrightarrow Sn + 2CO$$
$$ZnO + C \longrightarrow Zn + CO$$

- **Acidic flux** For basic impurities, acidic flux is added.

$$\underset{\text{(Acidic flux)}}{SiO_2} + \underset{\text{(Basic gangue)}}{FeO} \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

- **Basic flux** For acidic impurities, basic flux is added.

$$\underset{\text{(Limestone)}}{CaCO_3} \longrightarrow CaO + CO_2(g)$$

$$\underset{\text{(Basic flux)}}{CaO} + \underset{\text{(Acidic gangue)}}{SiO_2} \longrightarrow \underset{\text{(Slag)}}{CaSiO_3}$$

(ii) Other reducing agents: It is known as alumino thermic reduction or ***Gold Schmidt thermite process***. Aluminium powder is used for this purpose.

e.g., $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$

Mixture of the oxide and Al in the ratio of 3 : 1 is known as thermite and mixture of BaO_2 + Mg powder acts as ignition powder.

(iii) Auto reduction: This is used for reduction of sulphide ores of Pb, Hg, Cu, etc. The sulphide ore is heated in a supply of air at 770-970 K when the metal sulphide is partially oxidised to form its oxide or sulphate which then reacts with the remaining sulphide to give the metal.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$$

(B) Reduction of concentrated ores by other methods: Some metals cannot be obtained from their ores by using common reducing agents such as C, CO, H_2 etc. Other methods of reduction are used for such cases.

(i) Reduction by precipitation: Noble metals like silver and gold are extracted from their concentrated ores by dissolving

metal ions in the form of their soluble complexes.

$$Ag_2S + 4NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S$$

This solution is decanted off and treated with zinc to precipitate silver,

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag \downarrow$$

(ii) Electrolytic reduction or electrometallurgy: It is the process of extracting highly electropositive (active) metals such as Na, K, Ca, Mg, Al, etc by electrolysis of their oxides, hydroxides or chlorides in fused state, e.g., Mg is prepared by the electrolysis of fused salt of $MgCl_2$ ***(Dow's process).***

Refining or Purification of Crude Metals

- **Physical Methods (i) Liquation**: This method is used for refining the metals having low melting points (such as Sn. Pb, Hg, Bi) than the impurities; The impure metal is placed on the sloping hearth and is gently heated. The metal melts and flows down leaving behind the non-fusible impurities.

(ii) Poling: Poling involves stirring the impure molten metal with green logs or bamboo. The hydrocarbons contained in the pole reduce any metal oxide present as impurity. Copper and tin are refined by this method.

(ii) Distillation: Volatile metals like zinc and mercury are purified by distillation. The pure metal distils over, leaving behind non-volatile impurities.

(iv) Electrolytic Refining: In this method, impure metal forms the anode while the cathode is a rod or sheet of pure metal. The electrolytic solution consists of a soluble salt of the metal. On passing electricity, the pure metal gets deposited on the cathode while the insoluble impurities settle down below the anode as anode mud or anode sludge. Metals like Cu, Ag, Au, Cr, Zn, Ni, etc are purified by this method.

EXTRACTION OF Al, Fe, Cu, Ni AND Zn

1. **Metal Aluminium (Al):** Electrolysis of Al_2O_3 dissolved in molten Na_3A1F_6 (neutral flux). Neutral flux is the neutral compound added to the ore to decrease its melting point and to make it conducting, e.g., CaF_2, cryolite (Na_3AlF_6) etc.
2. **Metal Iron (Fe):** Reduction of the oxide with CO and coke in blast furnace. The iron obtained from blast furnace contains about 4% carbon and many impurities in smaller amount (e.g., S, P, Si, Mn) and is known as ***pig iron***.
   - **Cast iron**: It is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.
3. **Metal Copper (Cu):** Roasting of sulphide partially and reduction. Cu_2S + FeS is called matte. Blister copper contains 96-98% copper with small amounts of Ag and Au as impurity.
4. **Metal Zinc (Zn):** Roasting followed by reduction with coke. The metal may be purified by fractional distillation. 97-98% pure zinc is called spelter.
5. **Metal Nickel (Ni):** Roasting followed by Refining is done by ***Mond's Process***. Water gas is used as a reducing agent for nickel oxide.

$$2NiO + \underbrace{CO + H_2}_{\text{water gas}} \longrightarrow 2Ni + CO_2 + H_2O$$

Check Yourself

1. In Freundlich adsorption isotherm x/m = Kp1/n, the value of 'n' at low pressure is

(A) More than one. (B) Less than one.

(C) Equal to one. (D) From zero to one.

2. Which shape selective catalyst is used to convert alcohol to gasoline?

(A) Tripsin (B) Calgon

(C) ZSM-5 (D) Zeigler-Natta catalysts

3. Which one of the following is an example of adsorption?

(A) Ammonia in contact with water
(B) Anhydrous $CaCl_2$ with water

(C) Silica gel in contact with water vapours

(D) all of these

4. At 15°C out of H_2, CH_4, CO_2, NH_3, which gas will be adsorbed maximum by charcoal?

(A) H_2 (B) CH_4

(C) CO_2 (D) NH_3

5. Homogeneous catalysis does mean

(A) Reactants and goods have to be at the same level

(B) Catalyst and reactants must be in the same phase

(C)The reaction mixture must be formed homogeneously during

(D) The reaction mixture distribution must be homogeneous

Stretch Yourself

1. "Chemisorption is highly specific" Illustrate with an example.

2. Mention one shape selective catalyst used to convert alcohol directly into gasoline.

3. Name the catalyst used in the following process:

(a) Haber's process for the manufacture of NH_3 gas.

(b) Ostwald process for the manufacture of nitric acid.

4. Write the difference between:

(a) Catalysts and enzymes

(b) Promoters and poisons

5. Mention two important features of solid catalysts and explain them with the help of suitable examples.

Test Yourself

Question: State the sign of entropy change involved when the molecules of a substance get adsorbed on a solid surface.

Answer: when the molecules get adsorbed on a solid surface their RANDOMNESS decreases. This implies there will NEGATIVE entropy change. i.e., entropy decreases.

Answers

Check Yourself

Answer: 1(C); 2(C); 3(C); 4(D); 5(B)

Stretch Yourself

1. Do it by yourself.

2. ZSM-5 is the shape selective catalyst used to convert alcohol directly into gasoline.

3. Hint:

(a) Finely divided Fe/FeO, MO as a promoter.

(b) Pt (platinised asbestos)

4. Do it by yourself.

5. Heterogeneous catalyst involves the use of a catalyst in a different phase from the reactants. Typical examples involve a solid catalyst with the reactants as either liquids or gases. In heterogeneous catalyst the reactants are adsorbed on the to the surface of the catalyst at active sites. There is interaction between the surface of the catalyst and the reactant molecules are finally desorbed.